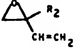
DEGS B05 83-736079/33 = J8 6013-706-B
S-carboxy-methyl-cysteine optical resolution - by selective crystallisation of the s- and r enantiomers from a supersaturated soln. of the ammonium salts of the mixed enantiomers
DEGUSSA AG 26.03.82-DE-211127
*D21 E16 (15.04.86) *DE3211127-C C07b-57 C07c-148/04 C07c-149/24*
24.03.83 as 048051 (280SC)
In the prodn. of S-(carboxymethyl) -(R)-cysteine (R-(I)) and S-(Carboxymethyl)-(S)-cysteine (S-(I)) from a mixt. of the two enantiomers, (A) the mixt. is dissolved in water in the presence of ammonia in an amt. such that the resulting soln. of the ammonium salts has a pH of 6-9; (B) the soln. is rendered supersatd. (C) one of the two enantiomers ammonium salts is crystallised by addn. of seed crystals of the ammonium salt of one of the enantiomers (provided that when the starting mixt. contd. an excess of one of the enantiomers, then the seed crystals added were of the ammonium salt of that enantiomer); (D) the pptd. crystals are sepd. off; (E) the ammonium salt of the other enantiomer is crystallised by adding seed crystals of this enantiomers ammonium salt to the mother liquor; (F) the pptd. crystals are again sepd., and (G) S-(I) or R-(I) is fixed from the corresp. ammonium salt.
Prods., esp. the (R)-enantiomer, are useful as pharmaceutical active substances, as well as in the cosmetics industry (e.g. in the prodn. of hair fixatives). (J58172365-A)(6pp)

RIKA B05 83-791052/43 = J8 6013-698-B
Alpha, beta-unsatd. ketone(e) mfr. - from carbon mon:oxide, hydrogen acetylene cpd. and olefin in presence of rhodium metal or pharmaceutical agrochemical
RIKAGAKU KENKYUSHO 02.03.82-JP-032537
*C03 E19 (15.04.86) *J58150533-A C07c-45/49 C07c-49/20 C07c-69/73 + B01j-23/46 B01j-31/16*
02.03.82 as 032537 (57WB)
Method comprises reacting CO, molecular, hydrogen, acetylene cpd. of formula R1-CC-R2 (where R1 and R2 are each H, alkyl, aryl, allyl, alkoxy carbonyl, acyl, alkoxyalkyl, or hydroxyalkyl gp.), and olefin cpd. of formula CH2=CH-R3 (where R3 is H, alkyl, alkoxycarbonyl, aryl, acyloxy, alkoxy gp., acyl gp., cyano gp., or halogen), in the presence of Rh metal or Rh cpd. catalyst to obtain alpha, beta-unsatd. ketone of formula R4CH=CR5-COR6 (where R4=R1 and R5=R2 or R4=R2 and R5=R1; R6 is -CH2CH2R3 or CHR3-CH3. The acetylene cpd. is e.g. acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, etc. The olefin cpd is e.g. ethylene, propylene, 1-butene, etc. The Rh cpd. is, e.g., Rh4(CO)12, Rh6(CO)16, Rh2(CO)4C12, etc.
Alpha,beta-unsatd. ketones are obtd. selectively and are useful as raw matls. for pharmaceuticals, agrochemicals, etc. (J58150533-A)(6pp)

SUMO B05 81-42377D/24 = J8 6013-690-B
Stereospecific prodn. of Z-isomers of allylic alcohol derivs. - from vinyl epoxide and organo-lithium cpd., useful intermediates for pharmaceuticals, agrochemicals, perfumes etc.
SUMITOMO CHEM IND KK 13.06.80-JP-080413
*C03 E19 (15.04.86) *EP-29603-A B01j-31/02 C07c-29/36 C07c-33/03*
13.06.80 as 080413 (CC)
Prodn. of predominantly Z-allylic alcohols of formula R1CH2CH:C(R2)CH2OH (I) comprises reacting epoxides (II) with an organolithium cpd. R1-Li (III) (where R1 is opt. substd., (un)branched 1-25C alkyl which can have one or more unsatd. bonds, pref. alkyl, alkenyl, aralkyl or 10C polycyclic hydrocarbyl; R2 is H or methyl).
Cpds. with R2 as methyl and R1 as sec-butyl, iso-butyl, cyclopropyl, cyclohexyl, 2-phenethyl or 2,2-ethylenedioxy-1,7-dimethy-bicycldimethyl bicyclo(2,2,1)heptyl-7-methyl are new.
USE/ADVANTAGE - (I) are useful as intermediates for pharmaceuticals, agricultural chemicals, perfumes etc. The Z-form of (I) is produced selectively in good yield in a single stage under mild reaction conditions. (J57007429-A)(6pp)



(II)

BLAS- B05 83-15329K/07 = J8 6013-684-B
Aryl-alkanoic acids prepn. by rearrangement of alpha-halo ketone(s) - in protic medium using non-noble metal salt catalyst
BLASCHIM SPA 23.07.81-IT-023085
*(15.04.86) *EP-71299-A B01j-27/13 C07b-41/08 C07c-57/32 C07c-59/64 C07c-69/61 C07d-333/24*
21.07.82 as 127434 (949RP)
Prepn. of alkanoic acids RR'RC-OOOY (I) comprises rearrangement of alpha-halo-ketones RCOCXR'R (II) in protic medium in the presence of a non-nonoble metal salt, hydrolysing the prod. if it is an ester to give the corresp. acid: (where R is opt. substd. aryl, opt. substd. heterocyclic or a fused arylheterocyclic system; R' and R are each H, 1-10C alkyl, benzyl or a value of R; X is halogen; and Y is H or 1-6C alkyl). Pref. protic medium is water or a 1-6C aliphatic alcohol. Pref. metal salts are of non-noble transition metals, esp. a Zn halide. Reaction may be in presence of a diluent.
(I) are useful as intermediates or as e.g. antiinflammatory, analgesic and antipyretic agents, esp. ibuprofen, fenclorac, indoprofen, naproxen, ketoprofen, tolmetin, etc. Other (I), e.g. thienyl acetic acid, may be used as intermediates to semi-synthetic penicillins or cephalosporins or other antiinflammatories, e.g. thiaprofen acid. The process avoids the use of expensive noble metal catalysts (see e.g. GB 2042543, J58024526-A) (4pp)

BANY B02 78-11067A/06 = J8 6013-479-B
Crystallisation of cephalexin hydrate - by contacting cephalexin with heated aq. soln. contg. (in)organic acid salt
BANYU PHARM CO LTD 14.06.76-JP-068768
*(14.04.86) *J52153991-A C07d-501/22*
14.06.76 as 068768 (38MD)
Process for crystallising prismatic crystals of cefalexin hydrate comprises contacting cefalexin with aq. soln. contg. salt of (in)organic acid (e.g. salt of HF, HCl, HBr, HNO3, HCOOH or AcOH, or a mixture esp. HCl) to form prismatic crystals of cefalexin hydrate. Temp. of the aq. soln. is 58 deg.C to temp.-necessary to allow crystallisation out of prismatic crystals of cefalexin hydrate from the aq. soln. (e.g. 57 deg.C at 6,000 ppm Cl(-); 30 deg.C at 42,000 ppm or 15 deg.C at 121,000 ppm). Aq. soln. is esp. 2-10% and 2-10 times w.r.t. wt. of cefalexin.
Process provides stable cefalexin crystals with little hygroscopicity and no static charge. (J52153991-A) (5pp)

ELIL B02 77-82879Y/35 = J8 6013-477-B
Cephalosporins prepn. from e.g. (3)-cephem sulphoxides - by using acyl bromide and bromine scavenger
ELI LILLY & CO 09.06.76-US-694516
*(14.04.86) *US4044002-A C07d-501/04*
08.06.77 as 068373 (1248WD)
Cephalosporin sulphoxides (I) are reduced to the corresp. cephalosporins (II) by treatment in an inert solvent at -25 deg.C to 50 deg.C with at least 2 molar equivs. per mole (I) of an acyl bromide R3COBr (where R3 is 1-10C alkyl opt. substd. by halogen, CN, Ph, 1-4C alkoxy or 2-5C alkoxycarbonyl, Ph opt. substd. by halogen, CN, NO2, 1-4C alkyl, 1-4C alkoxy or 2-5C alkoxycarbonyl; or 3-8C cycloalkyl) in presence of a Br scavenger. (I) is a 3-cephem or 3-exomethylene cepham cpd.
(II) are useful antibacterials and intermediates and they are obtd. by the efficient redn. of (I).
In an example, p-nitrobenzyl 7-phenoxyacetamido-3-methyl -3-cephem-4-carboxylate sulphoxide in CH2Cl2 contg. 2-methyl-2-butene was treated with acetyl bromide to reduce the sulphoxide. (J52151193-A)(17pp)

HOFF B05 76-97408X/52 = J8 6013-454-B
Carotenoid inters. prepn. from 3-alkoxy cycloalk 2-enones - by Grignard reaction with alkenyne derivs.
HOFFMANN-LA ROCHE AG 09.06.75-US-585224
*D13 E24 (14.04.86) *NL7606160-A C07c-45/67 C07c-49/64 C07c-173 C07f-09/54*
08.06.76 as 066163 (CC)
Prepn. of cyclic oxo cpds. is carried out by (a) reacting a cyclic ketone of formula (I) (where R is 3-8C alkyl; n = 0 or 1) with a Grignard reagent of formulae (IIa) or (IIb) (where Y is alkali metal or MgX; X is halogen; R1 is OH or a hydrolysable ether gp.) to form a prod. of formula (IIIa) or (IIIb); and (b) opt. converting the prod. into a carotenoid cpd. of formula (IV): (IV), viz. canthaxanthene (n = 1) and dinorcanthaxanthene (n = 0) are useful as food dyes. (J51149249-A)(18pp)

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